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MICROHARDNESS OF SOL-GEL FILMS WITH VARIOUS TEXTURES

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The effect of the regime of deposition (the rate of the deposition and the total content of film-forming oxides in the solution) on the microhardness of sol-gel films with a molar composition of 22% Bi₂O₃, 25% Fe₂O₃, and 53% TiO₂ is described. The mentioned parameters are shown to be connected with the particle size of the disperse phase of the film-forming solution, the degree of turbulence of its flow, and, supposedly, with the packing density of the solid particles in the film. It is shown that a correct choice of the regime for depositing the coating provides coatings of various thicknesses that possess maximum possible microhardness.

Thin-layer coatings that modify the surface of sheet technical glass and provide entirely new properties in them widen the range of application of such glass. Among the numerous methods for deposition of coatings the sol-gel technology is the simplest and least expensive one. The process consists in depositing a film-forming solution (FFS) on the glass sheet and subsequent drying and short-duration roasting of the part at a low temperature.

Glass filters that weaken the light flux in the requisite spectral range are created with the help of highly reflecting films of a specific thickness. The maximum value of the mirror reflectivity depends on the composition of the coating, and the position of the maximum specified by the functional part of the filter is determined by the thickness of the film. The latter increases with acceleration of the deposition and (or) increase in the concentration of the FFS, i.e., the total content of film-forming oxides in it [1]. Thus, by changing both parameters we can obtain glass filters that will reflect efficiently different spectral ranges from near ultraviolet to near infrared.

The service life of a glass part depends on its strength. The capacity of the surface to resist external mechanical actions is largely determined by the microhardness of the glass.

The question of how the thickness and the texture of films of identical composition affect the microhardness of the coated glass has virtually not been investigated.

We have studied a three-component film with a molar composition of 22% Bi₂O₃, 25% Fe₂O₃, and 53% TiO₂. The conditions of the preparation and deposition of the FFS, the roasting of the films, and the methods of their control are considered in [1]. The present paper concerns results of measurements of a large number of parallel specimens.

It is known that on the whole the microhardness of a material depends on the strength of the bonds realized in it [2].

It can be assumed that a green (not roasted) film is represented, by analogy with plastic clay materials, by a set of horizontal layers that consist of particles of the disperse phase of the FFS that are oriented differently with respect to each other, i.e., it has the form of a solid body possessing a certain packing density. If we assume that the particles of the solid phase are spherical and have the same size, then, obviously, the packing will be densest in the case when the particles of the subsequent layer are placed in the interspaces of the preceding one. This is possible when the glass specimen moves in the FFS at a speed that provides a steady flow of the liquid, which eliminates the appearance of eddies. In this very case, i.e., in a laminar flow, the disperse phase will move in parallel layers.

Roasting removes the moisture and the gaseous products of the decomposition of the initial materials from the green film; the particles of the solid phase sinter and, possibly, react with each other, forming a thin high-strength film. This process is influenced considerably by the size of the particles; it intensifies with diminution of the particles [3]. Therefore, the strength of the bonds in such a coating will be higher.

Consequently, we should start with finding out how the size of the particles of the disperse phase changes in solutions of various concentrations and assessing the flow of the sol under accelerated deposition of the coating.

Table 1 presents values of the pH, the viscosity of the FFS, and the moment when it begins to stabilize (the lifetime), determined visually by noticeable turbidity of the initially transparent solution. With increase in the concentration of the solution its kinematic viscosity increases proportionally, which agrees with the generally accepted concepts of the behavior of colloidal systems [4].

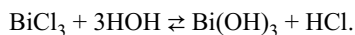
It is known that an increase in the content of the disperse phase in the sol promotes aggregation (coarsening) and ac-

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celerates sedimentation of the particles, i.e., the lifetime of the colloidal solution is inversely proportional to its concentration [4]. However, the results of Table 1 reflect the opposite phenomenon, i.e., a 1% FFS lives for 28 days and a 5% FFS lives for 51 days. This does not correspond to the universally accepted concept of the aggregate stability of disperse systems. This contradiction can be explained only by a decrease in the size of the sol particles with increase in its concentration. Indeed, in order to obtain a manufacture-adaptable and stable FFS we should reduce its pH with growth in the concentration, as is shown in Table 1.

A colloidal particle is represented by an aggregate of several microparticles of a difficultly soluble substance (the nucleus) enclosed in a layer of counter-ions [4]. Bismuth, titanium, and iron hydroxides, which form the nuclei of the sol particles in the studied system, begin to form under specific pH values that depend on the nature of the hydroxide. At the initial moment fine nuclei form, which coarsen progressively, lose their stability, and sediment. The closer the acidity of the solution to the pH of sedimentation of the hydroxide, the more rapid the process.

Hydrolysis of bismuth chloride occurs by the reaction



An increase in the number of OH^- ions (i.e., the content of water) shifts the reaction to the right, which is accompanied by intensification of the agglomeration and sedimentation of bismuth hydroxide. An increase in the content of hydrochloric acid (and hence a decrease in the pH) stimulates the reverse reaction, i.e., the sediment dissolves, and its volume fraction and the particle size decrease. Note that the hydrolysis of iron chloride and titanium alkoxide occurs in the same way.

The acidity of any FFS should be much less than the pH of maximum sedimentation of the disperse phase, because otherwise the solution will not be stable. It can be seen from Table 1 that the pH of the six solutions studied decreases progressively with growth in the concentration of the film-forming oxides, i.e., the size of a sol particle decreases gradually, and this should theoretically extend, and does extend, the lifetime of the solution.

With growth in the concentration of the studied sols their viscosity increases regularly. This can be caused by an increase in the volume fraction of the solid phase and (or) the degree of its dispersity [4], which is inversely proportional to the size of the particles. In our opinion, the second variant is more probable.

The hydrodynamics of a glass specimen moving in an FFS involves two stages simultaneously, namely, the motion of the flat plate in the flow of the solution and the motion of spherical particles of the solid phase in the flow of the solvent (ethanol).

It is known [5] that as a liquid flows over a flat plate positioned along the flow, the boundary layer thickens progres-

TABLE 1

Total mass content of film-forming oxides, %	Kinematic viscosity, $10^{-6} \text{ m}^2/\text{sec}$	pH	Life time, days
1	1.75	0.67	28
2	1.89	0.52	28
2.5	1.96	0.49	30
3	2.02	0.46	37
4	2.13	0.40	42
5	2.28	0.34	51

TABLE 2

Total mass content of film-forming oxides, %	Re/b for a rate of deposition of the coating, 10^{-3} m/sec				
	3	6	12	19	24
1	1.7/3.5	3.4/4.5	6.9/6.0	10.9/11.0	13.7/21.5
2	1.6/6.5	3.2/7.5	6.3/16.0	10.1/21.0	12.7/24.0
2.5	1.5/8.5	3.1/9.5	6.1/15.5	9.7/23.5	12.2/24.5
3	1.5/9.0	3.0/12.5	5.9/18.5	9.4/25.0	11.9/27.5
4	1.4/14.0	2.8/18.5	5.6/20.0	8.9/31.0	11.3/31.0
5	1.3/17.0	2.6/19.0	5.3/31.0	8.3/30.0	10.5/36.0

sively with increase in the distance from the front edge. As long as the local Reynolds number

$$\text{Re} \sim v/\nu,$$

where v is the speed of the flow and ν is the kinematic viscosity of the liquid, does not exceed a certain limit, the motion inside the layer is steady and the streamlines go parallel to the surface. When this limit is exceeded, the motion acquires a turbulent nature; at the critical point the boundary layer detaches from the body, leaving a domain of strong turbulence between it and the body. It can be assumed that this phenomenon is responsible for the worsening of the quality of the sol-gel film manifested by the appearance of a clear inhomogeneous band at the bottom edge of the glass, whose width depends on the regime of the deposition. Within this band the coating has a diminished covering power and a poor mirror brightness. In Table 2 the concentration of the solution and the rate of the deposition are compared with the width b of the nonuniform band at the bottom edge of the glass and the ratio v/ν , understood as a relative measure of the degree of turbulence of the flow.

With growth in the rate of deposition of an FFS with a fixed concentration the inhomogeneous band widens, which is accompanied by a regular progressive increase in the ratio v/ν . If the concentration of the FFS increases at a constant rate, the width of the band increases too, although the ratio v/ν decreases. This obvious contradiction to the principal laws of hydrodynamics is explainable by a decrease in the

TABLE 3

Total mass content of film-forming oxides, %	Rate of deposition of the coating, 10^{-3} m/sec	Film properties			
		thickness, Å	mean value of		confidence interval of the distribution of microhardness values, MPa
			refractive index	reflectivity, %	
1	3	190	2.00	20	7250 – 7030
	6	270	2.13	25	7500 – 7280
	12	300	2.13	34	7420 – 7220
	19	320	2.17	35	7840 – 7540
	24	360	2.16	35	7210 – 7010
2	6	360	2.14	41	7460 – 7160
	12	470	2.19	42	7340 – 7140
2.5	3	380	1.99	27	7500 – 7310
	6	450	2.28	45	7830 – 7530
	12	650	2.19	40	7120 – 6920
	19	790	2.18	39	6970 – 6770
	24	820	2.19	41	7080 – 6880
3	6	530	2.11	44	7120 – 6920
	12	820	2.14	36	7240 – 7040
4	3	520	1.98	35	7420 – 7220
	6	720	2.17	39	7800 – 7570
	12	1020	2.09	35	7580 – 7380
	19	1140	1.98	34	7300 – 7140
5	24	1380	1.95	31	6410 – 6210
	6	1100	2.06	34	6710 – 6400
	12	1380	1.88	24	6720 – 6530

size of the particles of the disperse phase in concentrated solutions. A friction force

$$F_{fr} \sim r,$$

where r is the particle radius, acts on each colloidal particle moving in the solvent [6].

When a glass plate with a constant mass m moves at a speed v , the applied force is

$$F = mv^2.$$

The resulting force acting on a sol particle is

$$\Delta F = F - F_{fr}.$$

At an invariable rate of deposition the value of F does not change, while F_{fr} decreases with growth in the concentration; consequently, the resulting force increases. This leads to intensification of the attraction of a spherical particle to the surface of the plate [5], which promotes densification of the packing on the one hand and acceleration of the motion of the particles and, hence, an increase in the local Reynolds number, on the other. The latter circumstance causes the observed growth in the size of the inhomogeneous band.

The sol particles in a turbulent flow should move over intertwining trajectories that constantly change their shape and penetrate the FFS in various directions [5]. Conversely, the particles in a laminar flow should move parallel to the

glass plate, which promotes regular and dense packing of them.

Whatever the density of the packing, gaps remain between the layers of spherical particles, and their size is proportional to the diameter of the particles. After roasting, these gaps continue to exist in the form of pores that penetrate and loosen [7] the thin film.

The porosity of the coating can be evaluated indirectly from the fluctuation of the refractive index, because it is known that for any porous body the refractive index is equal to [7]

$$n_{ef} = n_1 - P(n_1 - n_3) - (n_2 - n_3)f(P/P_0),$$

where n_1 , n_2 , and n_3 are the refractive indices of the substance composing the skeleton of the layer, the adsorbed water, and air, respectively; P is the porosity; $f(P/P_0)$ is the equation of the adsorption isotherm written in general form.

In addition, the mirror reflectivity of the film is related to its refractive index [8]. Consequently, the higher the porosity of the film, the lower its refractive index and mirror reflectivity.

Table 3 presents the physical properties and thickness of coatings obtained under various regimes of deposition. It can be seen that the changes in the refractive indices and reflectivities of the films obtained under progressively increased rates of deposition of 1%, 2.5%, and 4% FFS are the same; the values of the refractive index and the reflectivity increase progressively, attaining a maximum at a deposition rate of 19×10^{-3} m/sec for the 1% FFS and at 6×10^{-3} m/sec for the 2.5% and 4% FFS, and then decrease smoothly. The indicated regimes provide the least porous and hardest coating (7840 – 7540 MPa). This seems to be accompanied by the densest packing of the particles. Outside the mentioned regimes the porosity of the coatings seems to be higher due to the worsened packing density of the particles caused by an increase in the diameter of the particles of the concentrated solutions or a growing turbulence due to the acceleration of the deposition of the film.

The data of Table 3 confirm that the maximum possible microhardness of a film with a molar composition of 22% Bi_2O_3 , 25% Fe_2O_3 , and 53% TiO_2 is equal to 7840 – 7540 MPa. It is obvious that a correct choice of the deposition regime should provide maximum microhardness for a film of virtually any thickness. This is especially important since the functional region of maximum reflection is directly connected with the thickness of the coating.

The thickness range of the hardest films runs from 320 Å for a 1% FFS to 720 Å for a 4% FFS. An increase or a decrease in the concentration with respect to the mentioned range should most probably widen the thickness range. It should be taken into account that with increase in the concentration of the solution the deposition rate should be diminished in order to eliminate undesirable turbulence.

It can be seen from Table 4 that films of the same thickness obtained under different deposition regimes have differ-

TABLE 4

Total mass content of film-forming oxides, %	Rate of deposition of the coating, 10^{-3} m/sec	Film properties		
		thickness, Å	swelling in 0.1-N HCl	confidence interval of the distribution of microhardness values, MPa
1	24	360	11	7210 – 7010
2	6	360	2	7460 – 7160
2	12	470	0	7340 – 7140
2.5	6	450	0	7830 – 7530
2.5	24	820	2	7080 – 6880
3	12	820	0	7240 – 7040
4	24	1380	3	6410 – 6210
5	12	1380	0	6730 – 6530
2.5	19	790	10	6970 – 6770
4	6	720	8	7800 – 7570
3	6	530	8	7120 – 6920
4	3	520	0	7420 – 7220

ent values of the microhardness. The microhardness is higher the more concentrated the solution and the lower the deposition rate, i.e., the denser the packing and the less porous the coating.

The degree of porosity of the film can be evaluated from the swelling capacity under the action of aqueous solutions, for example, 0.1-N HCl. We determined this parameter as the ratio of the increment in the thickness of the film after a

30-min hold in a solution of hydrochloric acid to the thickness of the same coating after repeated roasting. It can be seen from Table 4 that the microhardness of the films is inversely proportional to its swelling capacity, which confirms the assumption made earlier.

The results obtained can be used to develop commercial technologies for modifying the surface of technical sheet glass.

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